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FACULTY OF ENGINEERING AND ARCHITECTURE

DEPARTMENT OF MATERIALS, TEXTILES AND CHEMICAL ENGINEERING
LABORATORY FOR CHEMICAL TECHNOLOGY

A THREE-PHASE ROBINSON-MAHONEY REACTOR AS A TOOL FOR INTRINSIC KINETIC MEASUREMENTS:

DETERMINATION OF GAS-LIQUID HOLD UP AND VOLUMETRIC MASS TRANSFER COEFFICIENT

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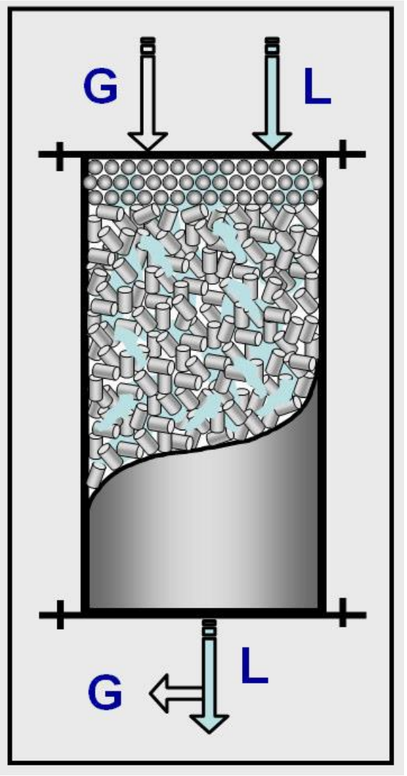
THREE-PHASE REACTIONS

- are **often encountered in chemical industry**, e.g., hydrotreating and hydrocracking in petroleum refining.

- typically, employ a **solid catalyst** to convert a **hydrocarbon liquid** under a **hydrogen atmosphere**. Small reaction products, such as ammonia, methane etc. will end up in the gas phase as well.

- **In industry**, these reactions are mostly performed in **trickle bed reactors**:
  - Fixed catalyst bed
  - Cocurrent down flow of the gas and the liquid phase
  - Adiabatic reactor
  - High temperature
  - High pressure



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LAB SCALE TESTING

Plug flow reactors

- Advantages
  - Ease of construction
  - Ease of operation
- Disadvantages
  - Flow pattern ideality difficult to realize
  - Complete catalyst wetting is unlikely
  - Mass transport limitations more likely

Mixed flow reactors

- Advantages
  - Flow pattern ideality
  - Complete catalyst wetting
  - Avoiding mass transport limitations
- Disadvantages
  - Long stabilization times
  - Moving equipment

Plug flow: practical reasons

Mixed flow: fundamental reasons

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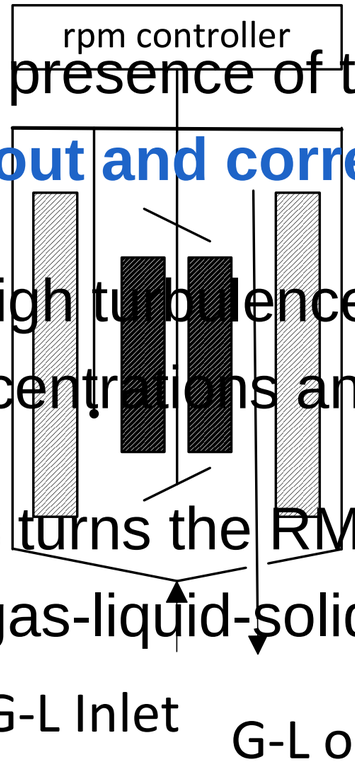
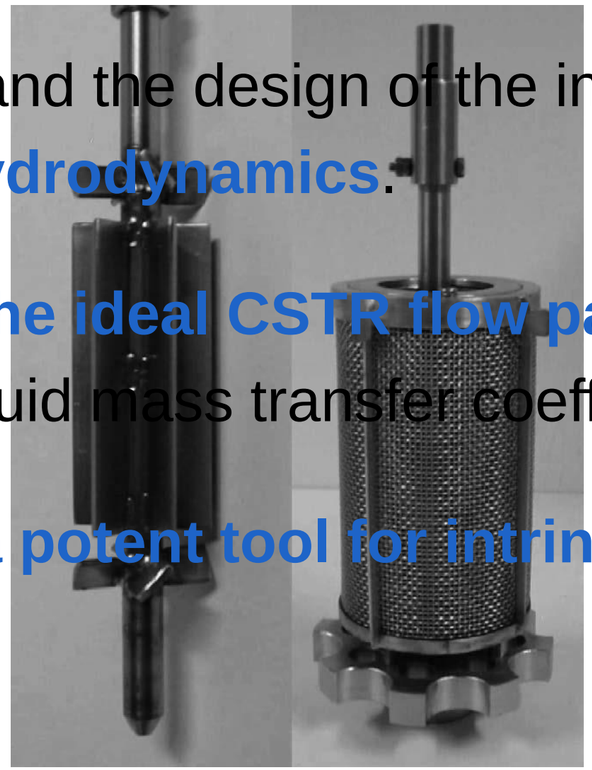
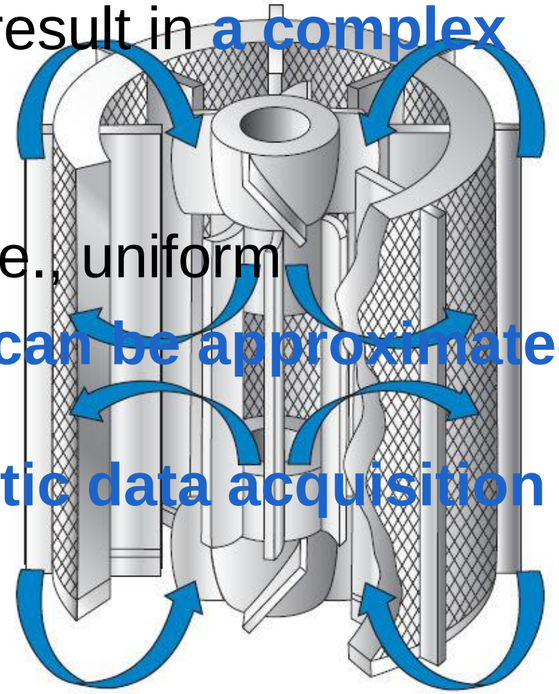
ROBINSON-MAHONEY (RM) REACTOR

- **A special type of fixed-basked CSTR** proposed by Mahoney et al. (1978) for three-phase reactions.



- The presence of three phases and the design of the internals result in **a complex lay-out and corresponding hydrodynamics**.
- At high turbulence conditions, **the ideal CSTR flow pattern**, i.e., uniform concentrations and high gas-liquid mass transfer coefficients, **can be approximated**.
- This turns the RM reactor into **a potent tool for intrinsic kinetic data acquisition** for gas-liquid-solid reactions.





Mahoney, J.A., Robinson, K.K., Myers, E.C., 1978, ChemTech 8, 758-763
Pitault, I., Fongarland, P., Koepke, D., Mitrovic, M., Ronze, D., Forissier, M., 2005, Chem. Eng. Sci. 60, 6240-6253
Santos-Moreaus, V., Brunet-Errard, L., Rolland, M., 2012, Chem. Eng. J. 207, 596-606
Raghuveer, C.S., Thybaut, J.W., De Bruycker, R., Metaxas, K., Berra, T., Marin, G.B., 2014, Fuel 125, 206-218
http://www.autoclave.com/

ROBINSON-MAHONEY (RM) REACTOR

- It is important to have an **adequate picture** of the **actual phase distribution in the reactor** and the **mass transport coefficient between the phases** in order to be able to correctly interpret the kinetic data obtained using the RM reactor.
- If the reactor composition is calculated using **a thermodynamic model** starting from the feed flow rates it **will reproduce the composition of the individual phases** but **the gas-liquid distribution will not be established correctly**. Hence, experimental investigations are necessary.
- Many **cold flow studies** have been performed. However, **extrapolation** to more severe temperature and pressure conditions **should be done with caution**.
- In this work, we **studied** the RM **at high temperature and pressure** mimicking industrial conditions **for the first time**.

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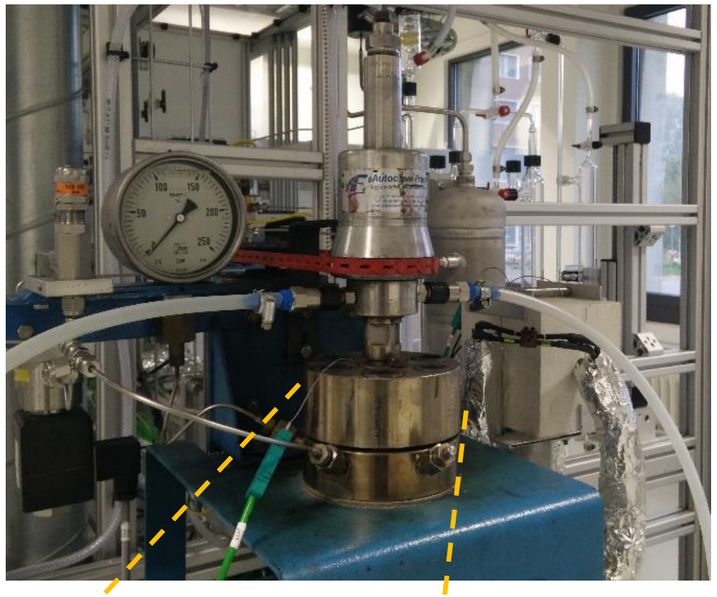
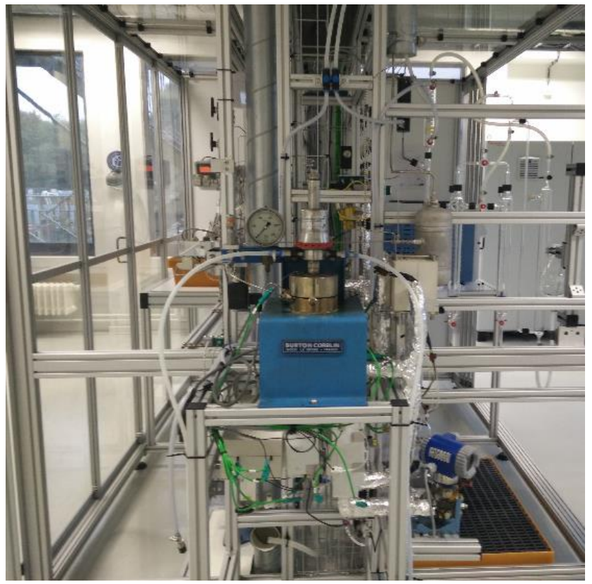
Pitault, I., Fongarland, P., Mitrovic, M., Ronze., D., Forissier, M., 2004, Catal. Today 98, 31-42
Pitault, I., Fongarland, P., Koepke, D., Mitrovic, M., Ronze, D., Forissier, M., 2005, Chem. Eng. Sci. 60, 6240-6253
Mitrovic, M., Pitault, I., Forissier, M., Simoens, S., Ronze, D., 2005, AIChE J. 51, 1747-1757

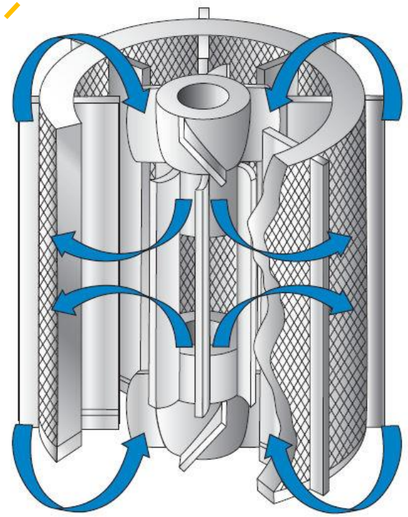
OUTLINE

- Introduction
- Experimental setup
- Liquid hold-up
- Volumetric gas-liquid mass transfer coefficient
- Conclusions

EXPERIMENTAL SETUP

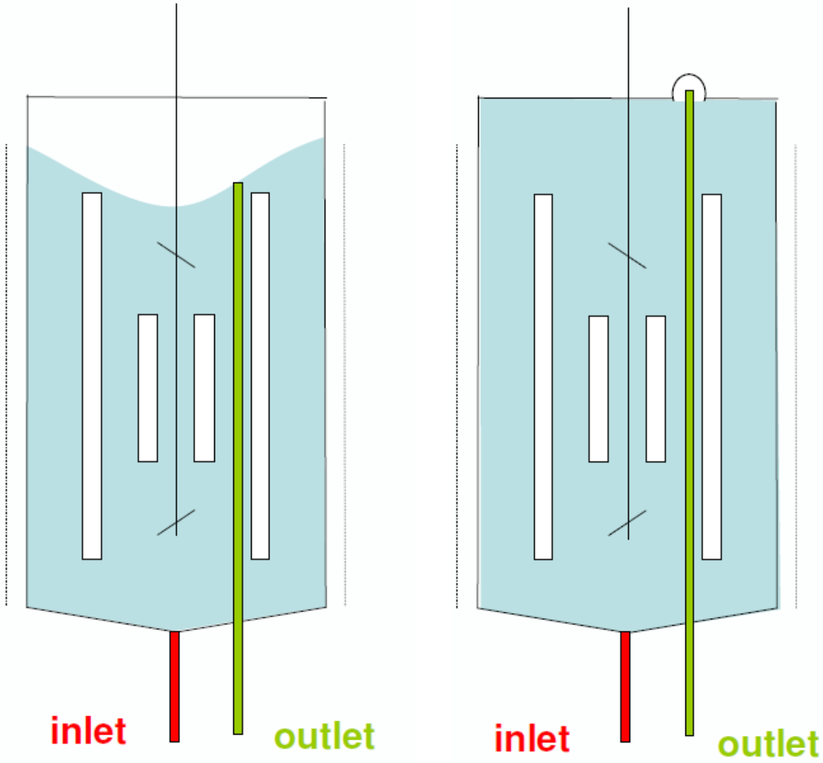






Characteristic	Dimension
Reactor volume	250 cm^3
Height of fixed annular catalytic basket	8.6 cm
Inner diameter of fixed annular catalytic basket	3.2 cm
Outer diameter of fixed annular catalytic basket	4.9 cm
Height of internal and external baffles	8.6 cm
Width of internal and external baffles	2 mm
Angle between two baffles	45°

Small modification allows to correctly **define the reaction volume**. Additionally, it guarantees a **complete and uniform mixing** without any separation between zones of continuous gas or liquid.



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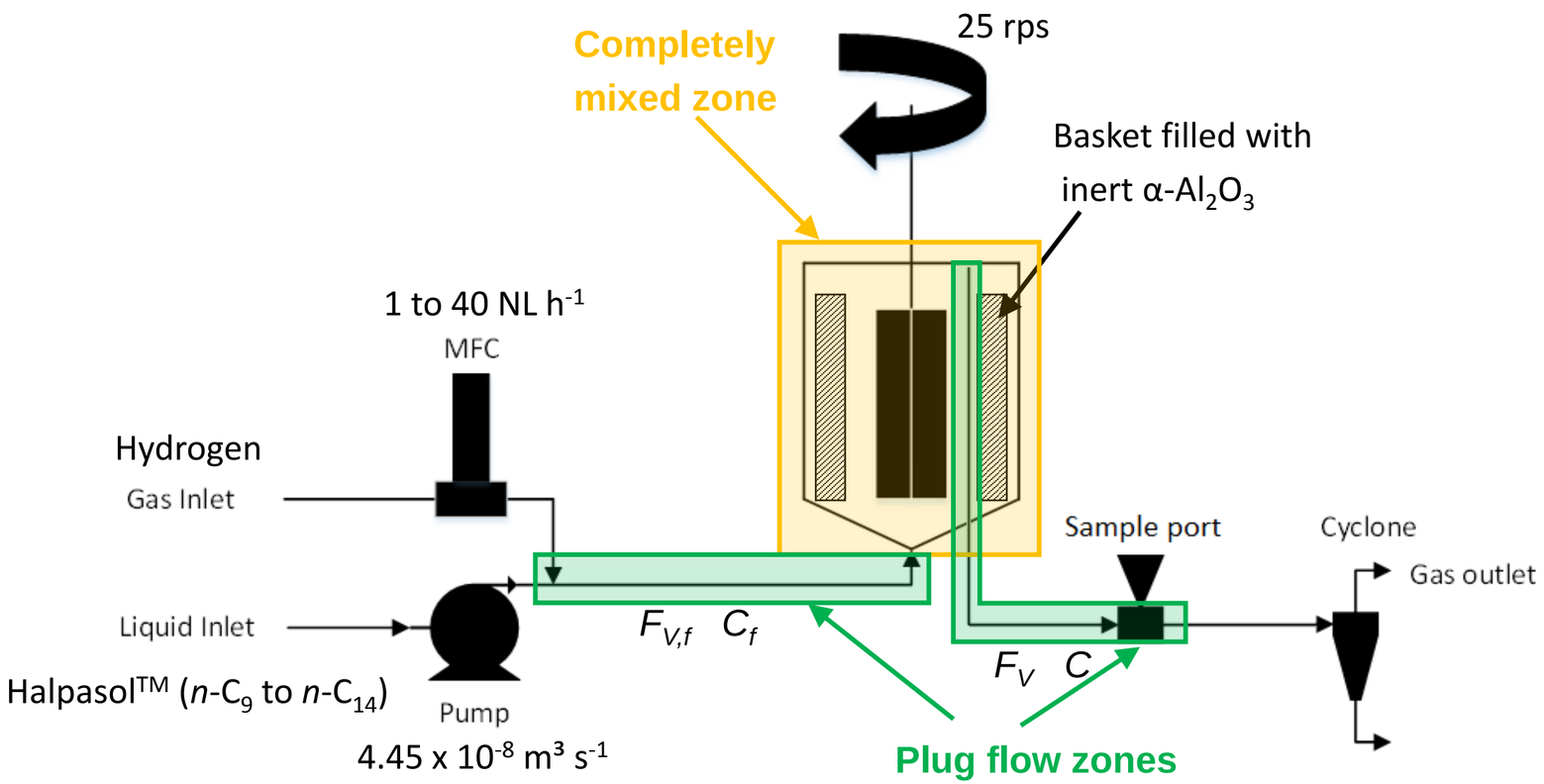
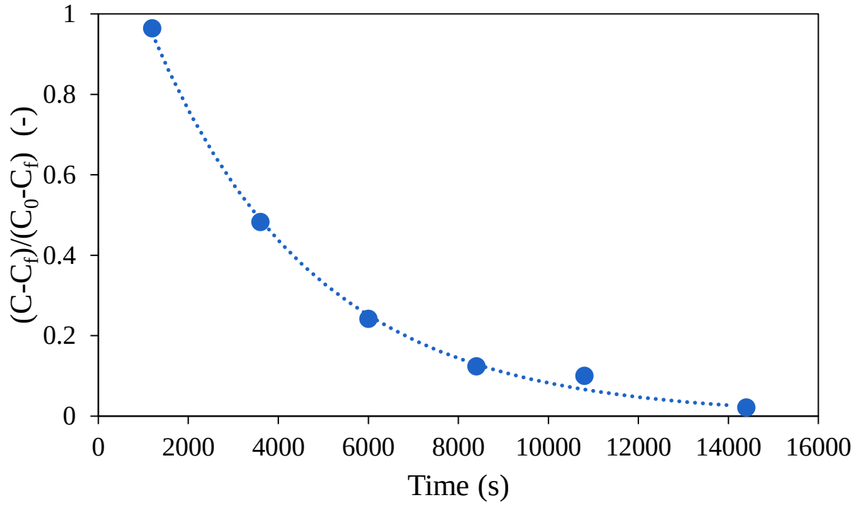
DETERMINING THE LIQUID HOLD-UP

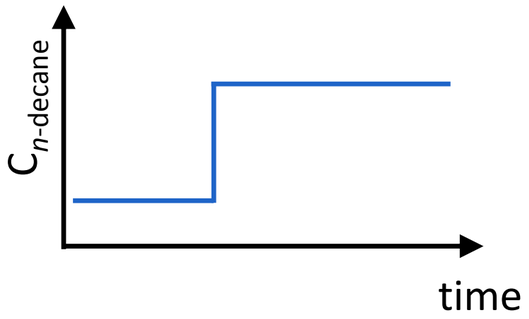




$$V_L \frac{\mathrm{d}C}{\mathrm{d}t} = F_{V,f} C_f - F_V C$$

$$\Rightarrow \quad C = C_f + (C_0 - C_f).\exp\left(-\frac{t}{\tau_L}\right)$$

Impose a step change to the concentration of *n*-C_{10}



Residence time: $\tau_L = \frac{V_L}{F_V}$ Liquid hold-up: $\varepsilon_L = \frac{V_L}{V_R} = \frac{\tau_L F_V}{V_R}$

Time: $t = t_{sampling} - t_{lag}$

$$\Rightarrow \quad \frac{C - C_f}{C_0 - C_f} = \exp\left(-\frac{(t_{sampling} - t_{lag})}{\frac{\varepsilon_L V_R}{F_V}}\right)$$

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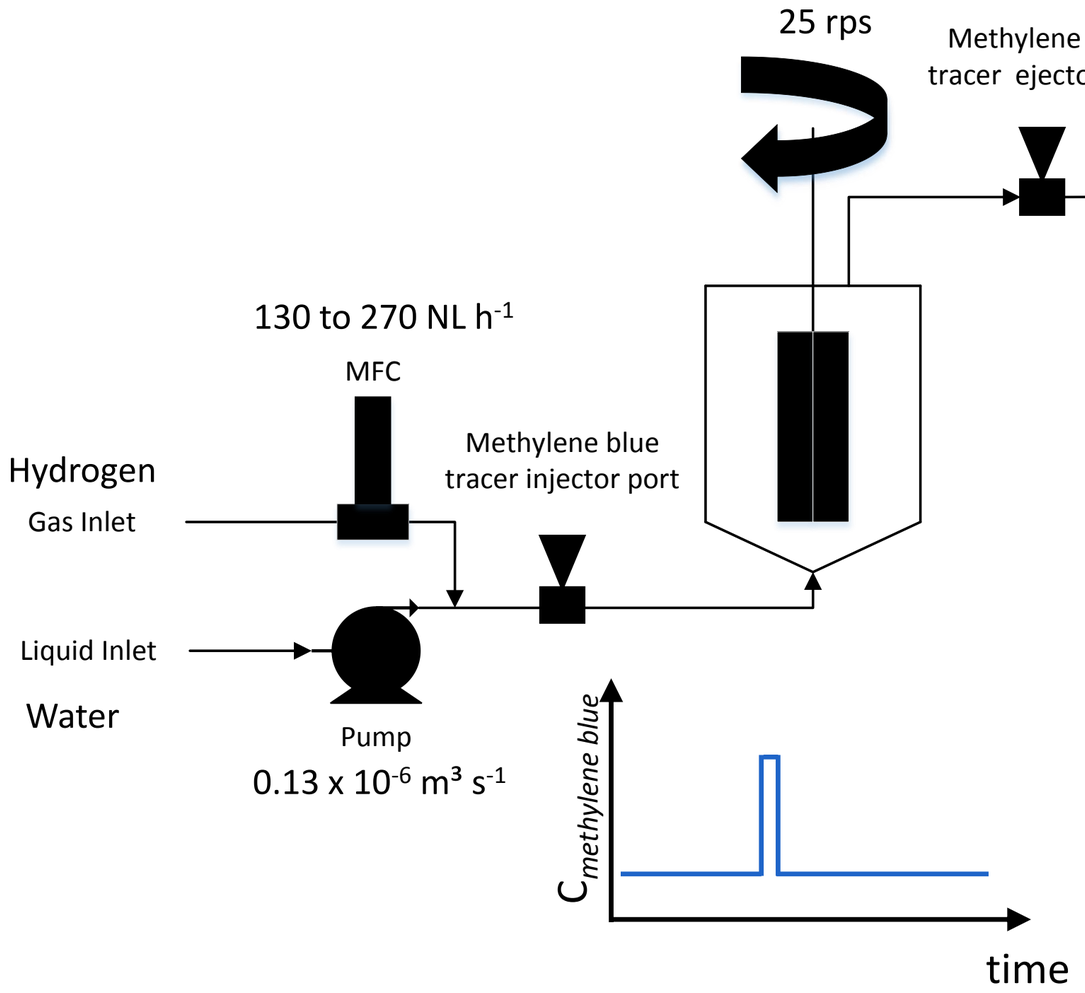
MODIFICATION FOR COLD FLOW



- A glass mock-up model reactor with identical dimensions
- Outlet at the top instead of an overflow
- No catalyst basket and pellets
- Water as liquid feed

Impose a pulse of methylene blue

$$\frac{C}{C_0} = \exp\left(-\frac{(t_{sampling} - t_{lag})}{\frac{\varepsilon_L V_R}{F_V}}\right)$$

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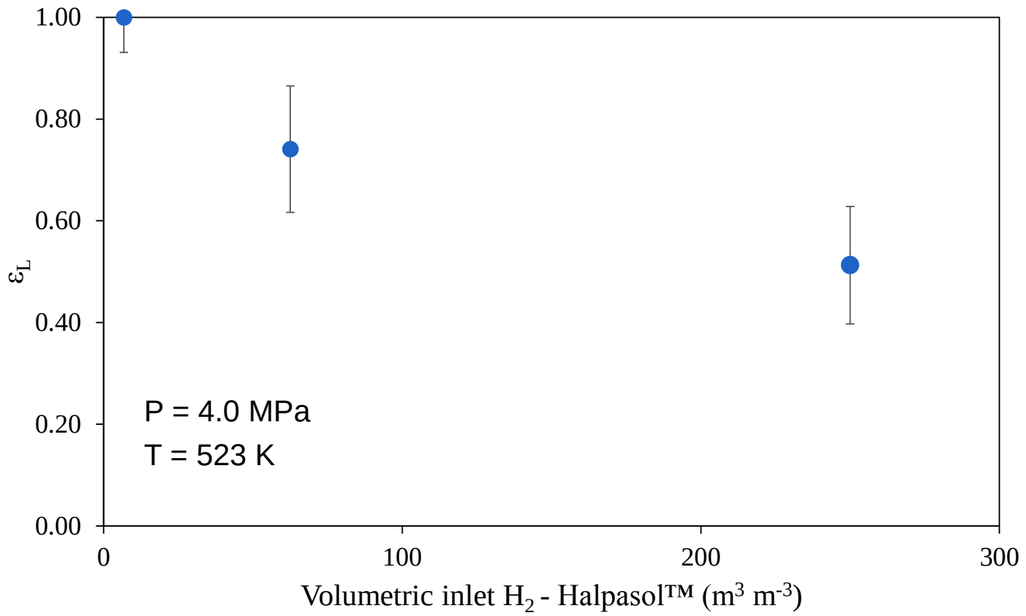
LIQUID HOLD-UP AT HTP CONDITIONS



Completely filled with liquid

↳ Dispersed gas bubbles in a continuous liquid phase

↳ Both gas and liquid constitute a continuous phase

↳ Liquid droplets dispersed in a continuous gas phase

The experimental liquid hold-up is clearly distinct from the one obtained using equilibrium calculations with the feed flow rates as input, *i.e.*, 50-100% compared to practically 0.

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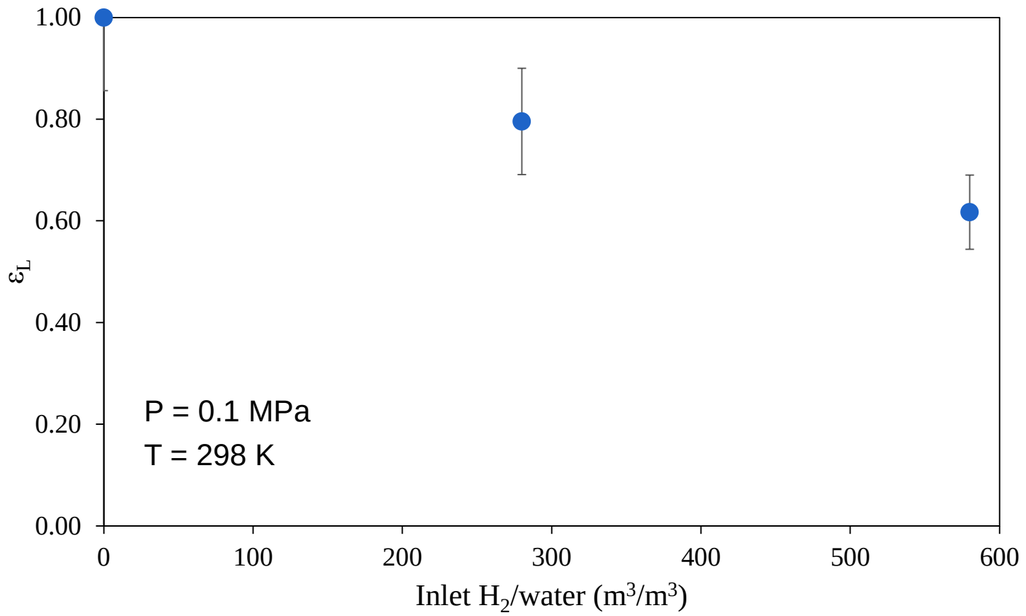
LIQUID HOLD-UP AT COLD FLOW



- A **similar trend** is observed at cold flow conditions
- The feed gas to liquid **ratio has to be increased much more** (about double) in order to obtain a **similar decrease**
- The **presence of gas bubbles** in a continuous liquid phase is **visually confirmed**
- The **number and size of the gas bubbles increases** with increasing inlet gas flow rates

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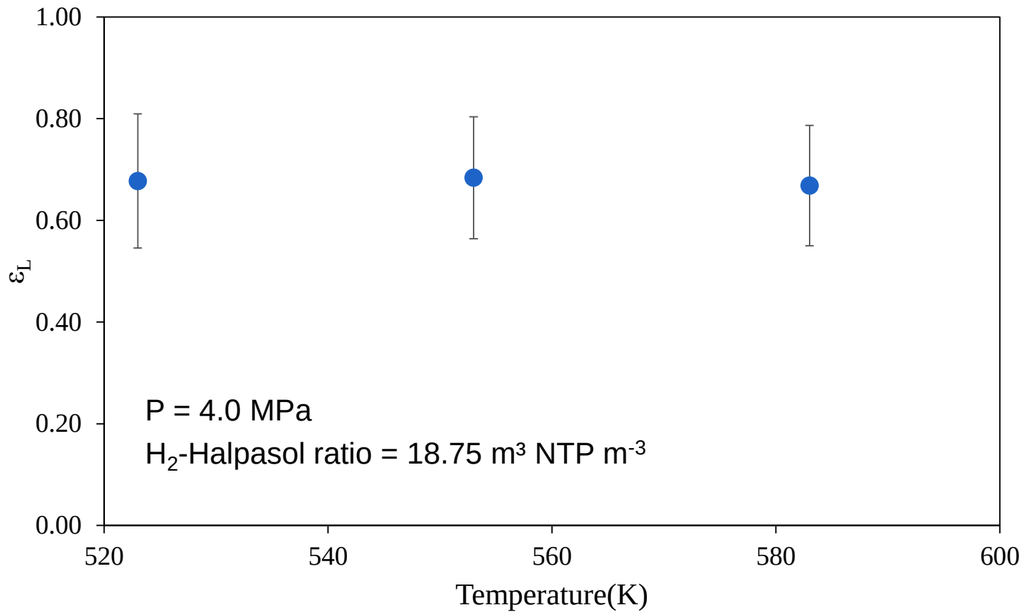
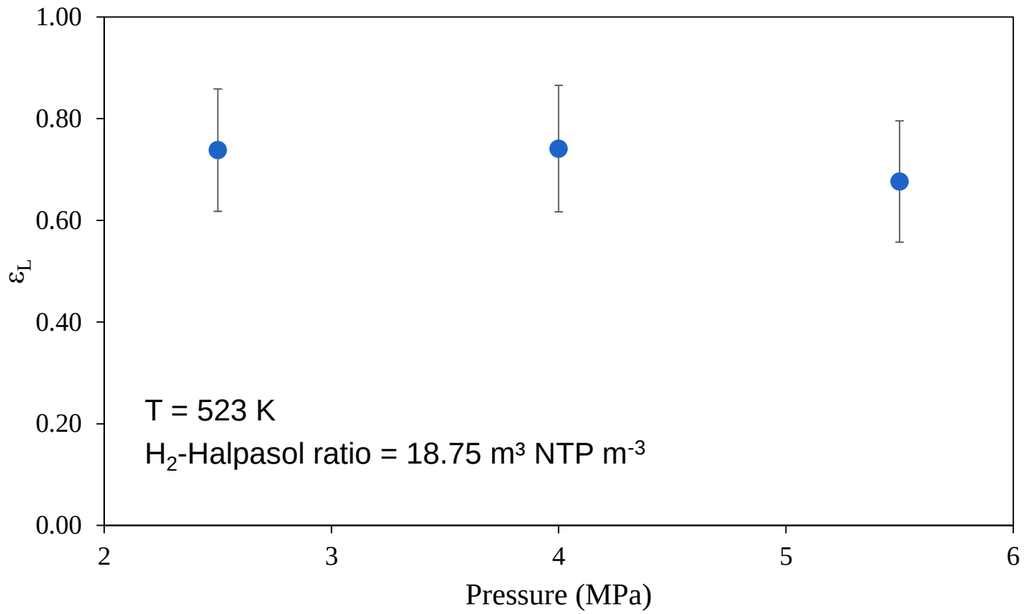
TEMPERATURE AND PRESSURE EFFECTS





- **Temperature** has **no significant effect** due to the low volatility of the liquid
- **Pressure** has **no significant effect** due to the non-compressibility of the liquid

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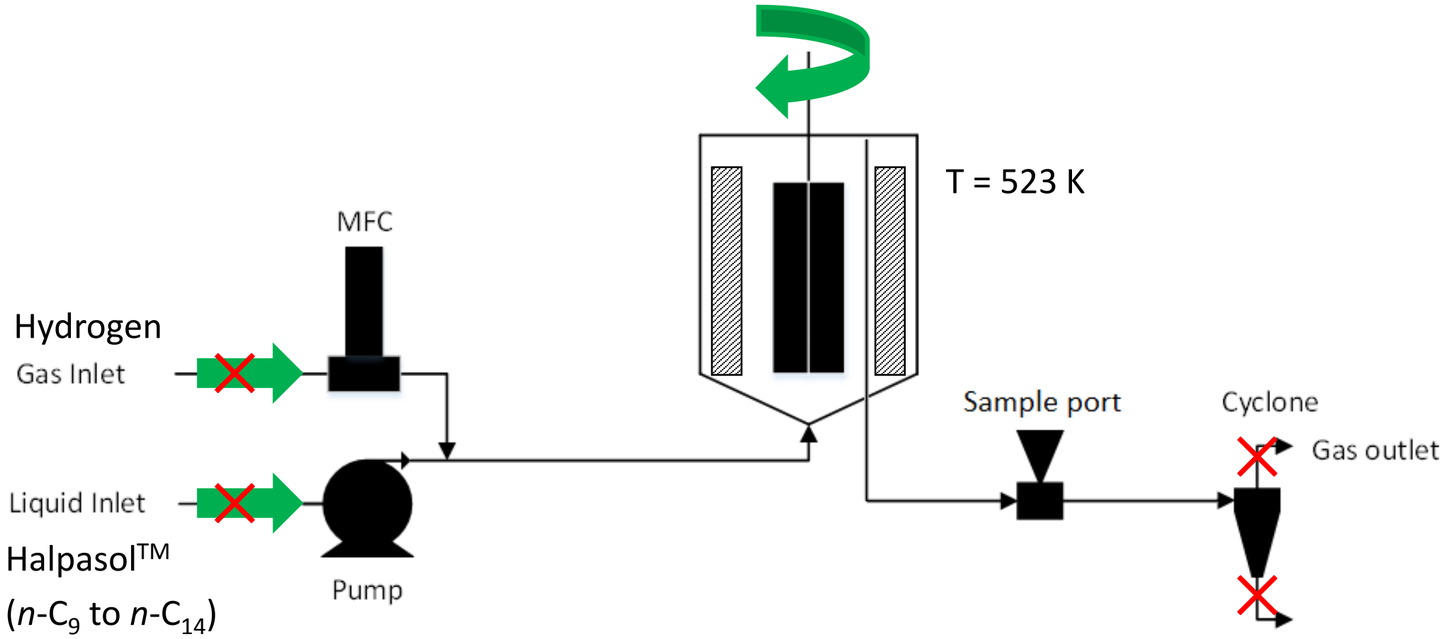
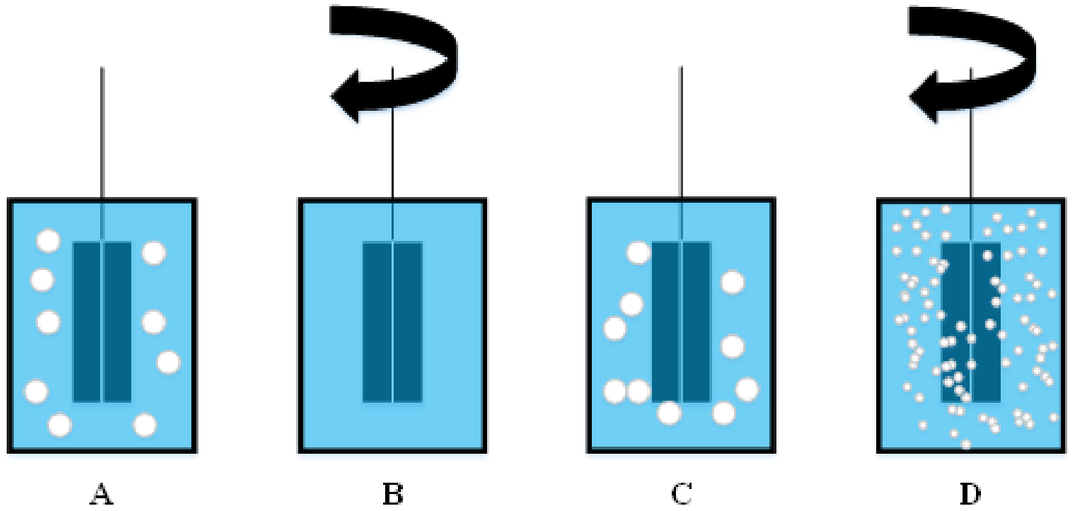
GAS-LIQUID MASS TRANSFER





Step A: Filling the reactor until liquid is observed at the outlet

Step B: Degassing until constant pressure (p_0)

Step C: Feeding gas until the desired pressure (p_m) is reached

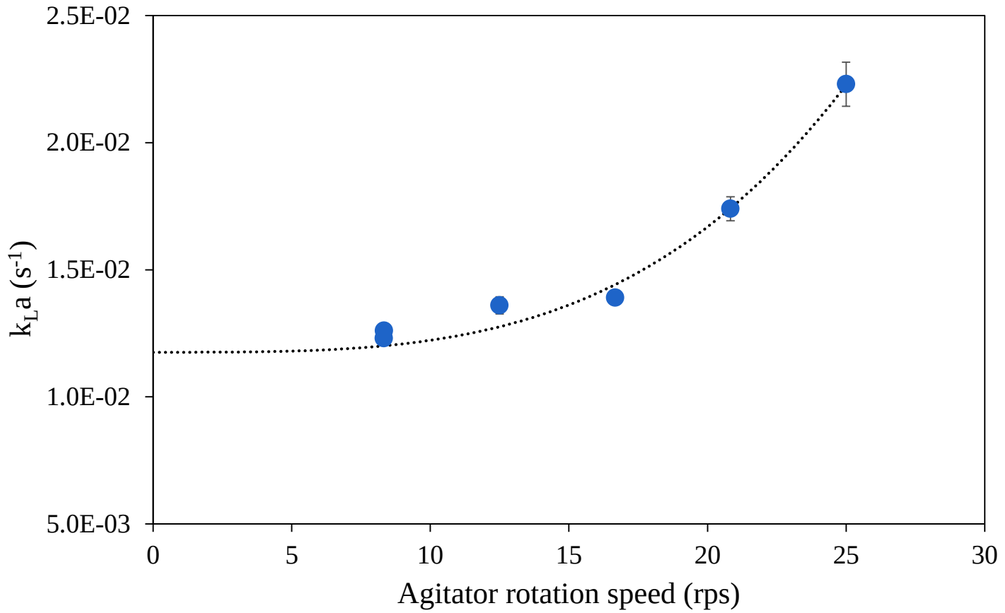
Step D: Monitoring the pressure ($p_m \rightarrow p_f$) decrease due to mass transfer

$$\frac{p_m - p_f}{p - p_f} = \exp\left(\frac{p_m - p_0}{p_f - p_0} k_L a.t\right)$$

Dietrich, E., Mathieu, C., Delmas, H., Jenck, J., 1992, Chem. Eng. Sci. 47, 3597-3604

Pitault, I., Fongarland, P., Koepke, D., Mitrovic, M., Ronze, D., Forissier, M., 2005, Chem. Eng. Sci. 60, 6240-6253

GAS-LIQUID MASS TRANSFER



Power number: $N_P = 6.57 - 54.771\left(\frac{b_t}{d_i}\right)$

Power input: $P = N_P \rho N_{agitator}^3 d_i^5$

$$\Rightarrow \quad k_L a = C_1 \left(\frac{P}{V}\right)^{C_2} + C_3$$

Parameter	Estimated value
C_1	$1.06 \times 10^{-2} \pm 0.12 \times 10^{-2}$
C_2^*	1.13
C_3	$1.17 \times 10^{-2} \pm 0.01 \times 10^{-2}$

* Value proposed by Pitault et al. (2005)

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Rutherford, K., Mahmoudi, S.M.S., Lee, K.C., Yianneskis, M., 1996, Chem. Eng. Res. Des., 74, 369-378
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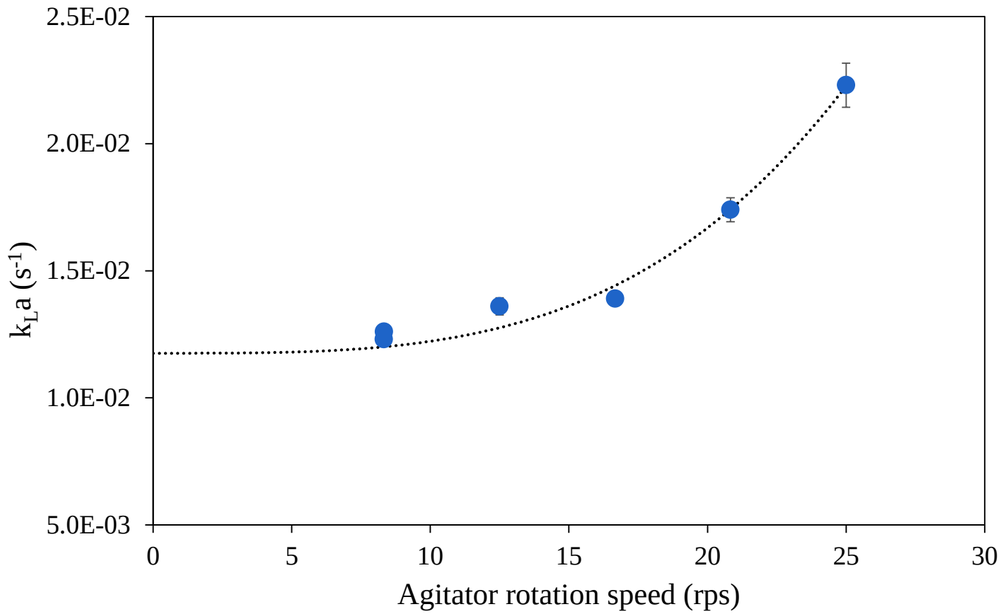
Pitault, I., Fongarland, P., Koepke, D., Mitrovic, M., Ronze, D., Forissier, M., 2005, Chem. Eng. Sci. 60, 6240-6253

GAS-LIQUID MASS TRANSFER



$$k_L a = C_1 \left(\frac{P}{V}\right)^{C_2} + C_3$$

Parameter	Estimated value
C_1	$1.06 \times 10^{-2} \pm 0.12 \times 10^{-2}$
C_2*	1.13
C_3	$1.17 \times 10^{-2} \pm 0.01 \times 10^{-2}$

* Value proposed by Pitault et al. (2005)

- Due to the **configuration** of the reactor and its internals **no stirring is necessary** to have **some mass transfer**
- **Initially**, the mass transfer only **increases moderately** due to a **minimum resistance induced by the reactor internals** (basked with very fine mesh filled with inert material)
- Once this resistance has been overcome, a **high turbulence regime** is entered where the mass transfer **increases more rapidly**
- At **higher agitator speeds**, a **maximum mass transfer** is expected

Pitault, I., Fongarland, P., Koepke, D., Mitrovic, M., Ronze, D., Forissier, M., 2005, Chem. Eng. Sci. 60, 6240-6253

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CONCLUSIONS

- A **three-phase bench-scale Robinson-Mahoney reactor is studied** for the first time using H_2 and Halpasol^{TM} **at high temperature and pressure** mimicking industrial conditions.
- The **liquid hold-up** of a low-volatile liquid did **not exhibit any variations with temperature and pressure**
- The liquid hold-up **decreased to 50%** when **increasing the inlet gas-liquid ratio** from 5 to 250 m^3 NPT m^{-3}
- **At ambient conditions**, the volumetric gas-liquid ratio had to be **increased to 580 m^3 NPT m^{-3} in order to observe a similar decrease**
- The **observed phase distribution** is in **distinct contrast** with the low liquid fractions calculated from **thermodynamic equilibrium calculations**

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CONCLUSIONS

- The evolution of the **volumetric gas-liquid mass transfer coefficient** with the power input per volume is **captured in the following correlation**:

$$k_L a = 1.06 \text{ x } 10^{-2} (P/V)^{1.13} + 1.17\text{x } 10^{-2}$$

- The **trend** as well as the **order of magnitude** are **similar to literature data obtained at ambient conditions**
- Albeit, in our case, the mass transfer **in the absence of stirring** is **higher** and the **variation** with the agitator speed is **less pronounced**
- Nevertheless, the obtained values indicate that, at high temperature and pressure conditions, the mass transfer in the RM reactor is **sufficiently high to ensure the measurement of intrinsic kinetics**

Thank you for your kind attention!

Acknowledgements: The research leading to these results has received funding from the European Union Seventh Framework Programme FP7/2007-2013 under grant agreement n° 238013 ‘MultiMod’. It has also been supported by the CAPITA ERANET programme via the IWT project n° 130900 ‘WAVES’. The authors would like to thank prof. Guy B. Marin, dr. Rasmus Boesen, ir. Jorgen Hoernaert and ir. Jeroen Poissonnier for their contributions during the course of this work.

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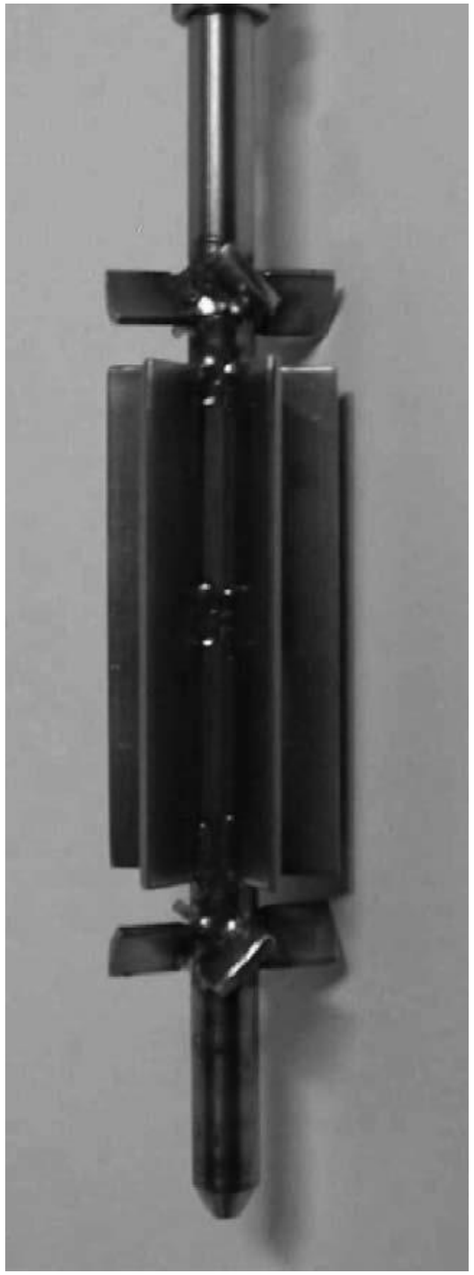

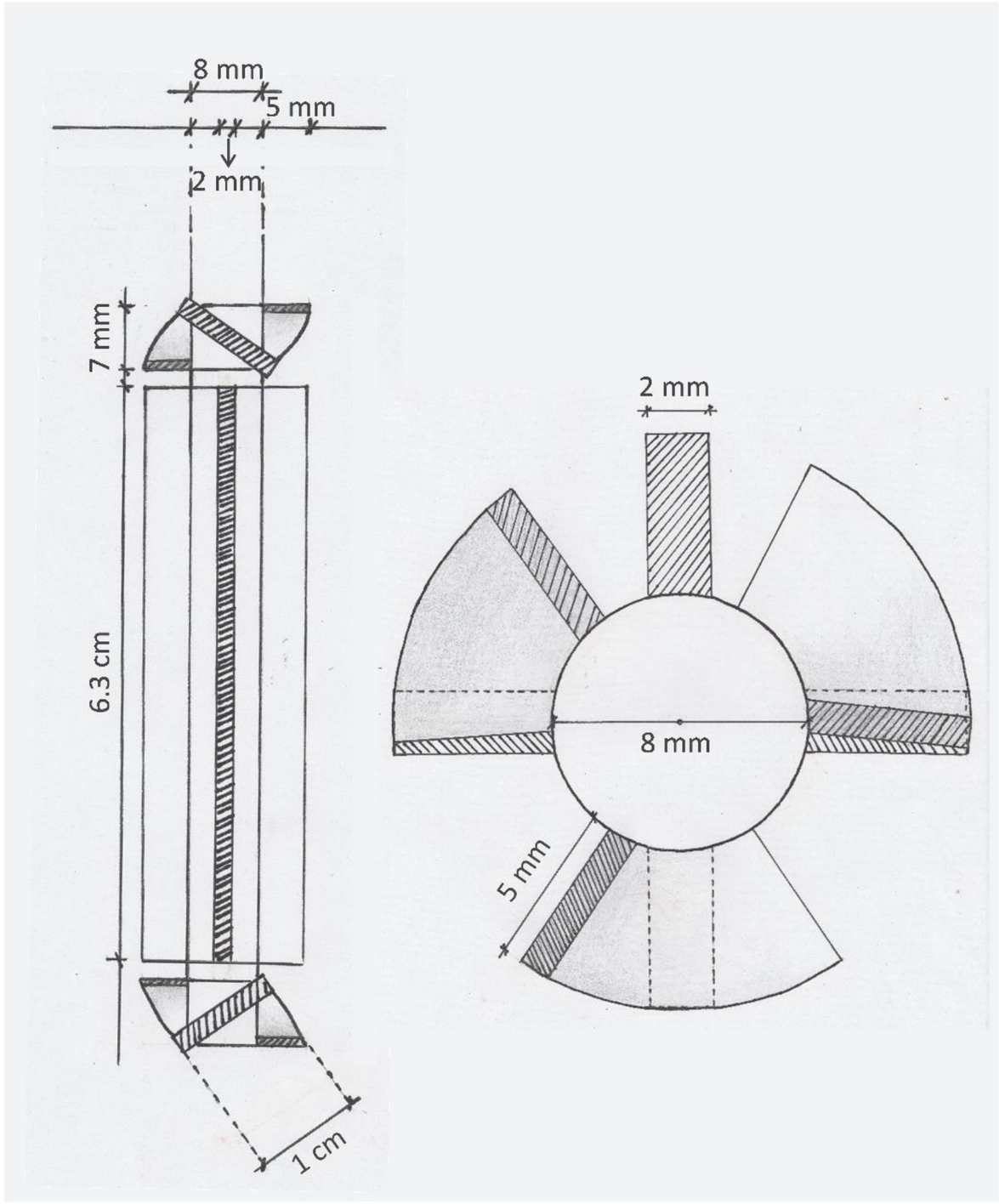

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